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Theoretical investigation of the nonadiabatic interactions and the translational factors in proton-hydrogen collisions

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The interaction in the (p^+, H) collision system is examined in terms of the exact H_2^+ and H electronic states. The nonadiabatic interactions between the H_2^+ electronic states which asymptotically go to the $n = 1$ or $n = 2$ atomic states are calculated together with the corresponding translational contributions. The question concerning the choice of the space-fixed and rotating atomic bases is investigated in relation to the long-range interactions. The adiabatic-diabatic question is discussed in connection with the noncrossing rule and dynamic correlations between the separated and united atomic states. With the aid of the calculated interactions, the "coupling hypothesis," which states that the nonadiabatic transitions are directly correlated with the closest approach of the electronic state energies, is examined. The characteristic features of the radial and rotational couplings are discussed in a phase-interference model.

I. INTRODUCTION

Current treatments of electronic transitions in heavy-particle atomic collisions utilize the Born-Oppenheimer separation in which a basis set of electronic states is adopted.[1] The interaction of the collision system is then visualized in terms of the adopted basis set of electronic states. The electronic basis sets which may be adopted are the atomic states, pseudostates, adiabatic molecular states, diabatic molecular states, etc. Formally all these basis sets are equivalent as long as the completeness properties of these sets are fully utilized. In practice where truncation is necessary, the suitability of a basis set depends critically on the collision system, the collisional process, the collisions energy, and numerical considerations. For this reason it is sometimes desirable to make use of more than one basis set to extend the suitability of the treatment.

A formulation which makes use of both the molecular and atomic electronic basis states has been developed by Chen and Watson.[2]

The formulation for heavy-particle collisions, regardless of the electronic basis set adopted, yields a set of second-order differential-integral equations for the nuclear motion. The use of the eikonal approximation permits the equations to be reduced, independent of trajectory considerations, to a set of first-order differential equations for the eikonal amplitudes Q_α.

$$\frac{dQ_\alpha(z,\vec{B})}{dz}=\sum_{\beta\neq\alpha}\Lambda_{\alpha\beta}(z,\vec{B})Q_\beta(z,\vec{B}) + (\text{boundary conditions})\,, \tag{1.1}$$

where α and β are channel labels and the functions $\Lambda_{\alpha\beta}$ are expressed in terms of the nondiagonal coupling interactions and eikonal phases coming from the diagonal interactions. Thus all the dynamics of the collision system are in $\Lambda_{\alpha\beta}$. For straight-line trajectories, we have simply

$$\Lambda_{\alpha\beta}(z,\vec{B})=i\mathcal{V}_{\alpha\beta}(z,\vec{B})\exp\left(i\int^{z}(\kappa_\alpha-\kappa_\beta^*)\,dz'\right) \tag{1.2}$$

with the local momenta given by

$$\kappa_\alpha=(k_\alpha^2-2m\mathcal{V}_\alpha)^{1/2} \tag{1.3}$$

where the diagonal interactions $\mathcal{V}_\alpha$ and the nondiagonal coupling interactions $\mathcal{V}_{\alpha\beta}$ depend on the electronic basis states adopted and on the details of the formulation.

The importance of molecular electronic states (defined in the Born-Oppenheimer separation approximation) in heavy-particle collisions is clearly demonstrated by the qualitative success[3] of the promotion model of Fano and Lichten.[4] In using such molecular electronic states for a quantitative description of the collisions, one often chooses to express the electronic states in a set of coordinates which is moving with the molecular axis. Such a choice greatly simplifies the determination of the molecular electronic states. This simplification, however, gives rise to several peculiarities. (i) The asymptotic scattering and rearrangement channels can be rigorously defined only in terms of an infinite number of states. (ii) The interactions which come primarily from the coupling of the electronic and nuclear motions (i.e., the nonadiabatic interactions) have unphysical long-range behaviors. These peculiarities have caused some difficulties in the "perturbed stationary-state" method[5] and lead to the introduction of *ad hoc* translation factors[6] in the description of the asymptotic states.

These peculiarities, due to the choice of coordinates used in describing the molecular electronic states, are removed by proper coordinate transformations in the formulation of Chen and Watson.[2] The unphysical long-range interactions are eliminated by the coordinate transformation of the kinetic-energy operators. The coordinate transformation of the channel wave functions give rise to the translational factors. An attractive feature of this formulation is that the translational factors are naturally defined and are separable from the matrix elements involving the molecular electronic states. This separability which is accomplished by the combined use of molecular and atomic basis states is not unexpected since the translational factors belong to the asymptotic behavior where the molecular electronic states essentially merge into atomic states.

The purpose of the present work is to investigate the interactions in heavy-particle collisions as expressed in terms of molecular and atomic electronic states. The questions of interest are: (1) What are the important features of the nonadiabatic interactions; (2) To what extent is the hypothesis that nonadiabatic transitions are directly correlated to the distance of closest approach of the electronic state energies correct; and (3) What is the role of the translational factor in the interactions of the system. A study of the interactions can be carried out unambiguously for the proton-hydrogen collision system since for this system exact solutions are available for the asymptotic atomic states and for the adiabatic H_2^+ molecular electronic states. In addition, the translational factor contributions for the (p^+, H) system can be evaluated in closed forms—a consequence of the separability of the translational factor from the molecular electronic matrix elements.

The plan of the paper is the following. In the next section, the notations and coordinate systems to be used are defined as the explicit expression for the interactions $\mathcal{V}_{\alpha\beta}$ are presented and analyzed. These interactions consist primarily of nonadiabatic interactions expressed in terms of the adiabatic molecular electronic states and of translational-factor contributions expressed in terms of the asymptotic atomic states.

The evaluation of the nonadiabatic interactions is considered in Sec. III. The evaluation was performed in three steps: (1) the generation of the adiabatic H_2^+ electronic states, (2) the calculation of the nonadiabatic electronic matrix elements and (3) the analytic evaluation of the asymptotic nonadiabatic interactions. A discussion on the choice of the space-fixed or the rotating asymptotic atomic basis is given in connection with the long-range behavior of the nonadiabatic interactions. The results are presented in graphic form.

In Sec. III the translational-factor contributions are evaluated. The closed expressions for the matrix elements of the translational factor are given in terms of the space-fixed atomic basis set. The detailed relationship between the space-fixed and the rotating molecular-axis atomic basis sets is then examined. The transformation of the coupled equations from the space-fixed atomic basis to the rotating atomic basis is given in the Appendix. The effect of the translational-factor contributions on the nonadiabatic interactions is investigated as a function of the relative nuclear velocity. The residual zero-velocity contribution of the translational factors is pointed out.

In Sec. IV, we discuss with the aid of the calculated interactions the current coupling hypothesis, the question of noncrossing rules, and the adiabatic and diabatic representations. Based on the qualitative features of the radial and rotational couplings, a simple phase-interference model is presented.

II. INTERACTIONS IN THE (p^+,H) COLLISION SYSTEM

In this section we summarize the formulation of Chen and Watson[2] for the (p^+, H) collision involving the processes $[(e^-, p^+) \Rightarrow H]$

$$p^+ + (e^-, p^+) \to p^+ + (e^-, p^+) \qquad (2.1a)$$

$$\to (p^+, e^-) + p^+ . \qquad (2.1b)$$

An appropriate coordinate system for the scattering channel (2.1a) is defined by the center-of-mass variables $(\vec{R}_1, \vec{r}_1)$, where $\vec{R}_1$ is the vector from the center of mass of the target to the incident proton, and $\vec{r}_1$ is the vector from the target proton to the electron. For the rearrangement channel (2.1b), the appropriate coordinate system is defined by the center-of-mass variables $(\vec{R}_2, \vec{r}_2)$, where $\vec{R}_2$ is the vector from the target proton to the center of mass of the incident proton and the transferred electron, and $\vec{r}_2$ is the vector from the incident proton to the electron. The molecular states for the (p^+, H) system are most easily calculated in the coordinate system defined by the center-of-mass variables $(\vec{R}_0, \vec{r}_0)$, where $\vec{R}_0$ is the vector from the target proton to the incident proton, and $\vec{r}_0$ is the vector from the center of mass of the two protons to the electron. The relations between these coordinate systems which are shown in Fig. 1 are

$$\vec{R}_0 = \vec{R}_1 + \frac{m}{m+M}\vec{r}_1 = \vec{R}_2 - \frac{m}{m+M}\vec{r}_2\,, \tag{2.2a}$$

$$\vec{r}_0 = -\tfrac{1}{2}\vec{R}_1 + \frac{m+2M}{2(m+M)}\vec{r}_1 = \tfrac{1}{2}\vec{R}_2 + \frac{m+2M}{2(m+M)}\vec{r}_2\,. \tag{2.2b}$$

The Hamiltonian for the (p^+, H) system is

$$H = T + V_1 + V_2 + V_{12} \tag{2.3}$$

where T is the center-of-mass kinetic-energy operator, V_1 and V_2 are, respectively, the interaction potentials of the electron with target and incident protons, and V_{12} is the interaction between the protons. The kinetic-energy operator may be expressed in each of the three coordinates

$$\begin{aligned} T &= -\frac{1}{2M_0}\nabla^2_{\vec{R}_0} - \frac{1}{2\mu_0}\nabla^2_{\vec{r}_0} \\ &= -\frac{1}{2M_1}\nabla^2_{\vec{R}_1} - \frac{1}{2\mu_1}\nabla^2_{\vec{r}_1} \\ &= -\frac{1}{2M_2}\nabla^2_{\vec{R}_2} - \frac{1}{2\mu_2}\nabla^2_{\vec{r}_2} \end{aligned} \tag{2.4}$$

with

$$\begin{aligned} &M_0 = \tfrac{1}{2}M\,, \quad M_1 = M_2 = \frac{M(m+M)}{m+2M}\,, \\ &\mu_0 = \frac{2mM}{m+2M}\,, \quad \mu_1 = \mu_2 = \frac{mM}{m+M}\,, \end{aligned} \tag{2.5}$$

where m is the mass of the electron and M is the mass of the proton.

The channel Hamiltonian for the scattering channel is

$$\mathcal{H}_1 = K_1 + h_1 \tag{2.6a}$$

with

$$K_1 = -(1/2M_1)\nabla^2_{\vec{R}_1}\,, \tag{2.6b}$$

$$h_1 = -(1/2\mu_1)\nabla^2_{\vec{r}_1} + V_1(r_1)\,. \tag{2.6c}$$

The asymptotic atomic states of the target hydrogen are eigenstates g_α of h_1

$$h_1(\vec{r}_1)g_\alpha(\vec{r}_1) = W_\alpha g_\alpha(\vec{r}_1)\,. \tag{2.7}$$

Similarly, the channel Hamiltonian for the rearrangement channel is

$$\mathcal{H}_2 = K_2 + h_2 \tag{2.8a}$$

with

$$K_2 = -(1/2M_2)\nabla^2_{\vec{R}_2}\,, \tag{2.8b}$$

$$h_2 = -(1/2\mu_2)\nabla^2_{\vec{r}_2} + V_2(r_2)\,. \tag{2.8c}$$

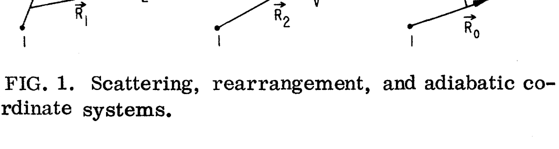

FIG. 1. Scattering, rearrangement, and adiabatic coordinate systems.

The asymptotic atomic states of the product hydrogen are eigenstates f_α of h_2

$$h_2(\vec{r}_2)f_\alpha(\vec{r}_2) = W_\alpha f_\alpha(\vec{r}_2)\,. \tag{2.9}$$

The molecular electronic states for the (p^+, H) system are usually expressed in terms of the center-of-mass variable $(\vec{R}_0, \vec{r}_0)$. We have for the Hamiltonian

$$H = K_0 + h_0 \tag{2.10a}$$

with

$$K_0 = -(1/2M_0)\nabla^2_{\vec{R}_0}\,, \tag{2.10b}$$

$$h_0 = -(1/2\mu_0)\nabla^2_{\vec{r}_0} + V_1 + V_2 + V_{12}\,. \tag{2.10c}$$

The eigenstates φ_α of the electronic Hamiltonian h_0 are the adiabatic $\mathrm{H_2}^+$ electronic states

$$h_0\varphi_\alpha(\vec{r}_0, \vec{R}_0) = w_\alpha(\vec{R}_0)\varphi_\alpha(\vec{r}_0, \vec{R}_0)\,. \tag{2.11}$$

These adiabatic electronic states in the $R_0 \to \infty$ limit go over to a linear combination of atomic states centered at the protons. A linear combination of φ_α may be constructed,

$$\varphi'_\alpha(\vec{r}_0, \vec{R}_0) = \sum_\beta c_{\alpha\beta}\varphi_\beta(\vec{r}_0, \vec{R}_0) \tag{2.12}$$

so that asymptotically φ'_α goes over to atomic states centered at the appropriate proton. We have

$$\lim_{R_0\to\infty} \varphi'_\alpha(\vec{r}_0, \vec{R}_0) = g'_\alpha(\vec{r}\,'_1) = R_{nl}(r_1)Y_{lm}(\hat{r}'_1)\,, \tag{2.13a}$$

$$\lim_{R_0\to\infty} \varphi'_\beta(\vec{r}_0, \vec{R}_0) = f'_\beta(\vec{r}\,'_2) = R_{nl}(r_2)Y_{lm}(\hat{r}'_2)\,, \tag{2.13b}$$

where $R_{nl}(r_i)$ are the radial hydrogenic wave functions and $Y_{lm}(\hat{r}'_i)$ are the spherical harmonics. The prime on $\hat{r}_i$ in the spherical harmonics is to remind us that $\hat{r}'_i$ depends on $\vec{R}_0$. Thus atomic states $g'_\alpha(\vec{r}\,'_1)$ and $f'_\alpha(\vec{r}\,'_2)$ differ from $g_\alpha(\vec{r}_1)$ and $f_\alpha(\vec{r}_2)$ of Eqs. (2.7) and (2.9) by the $\vec{R}_0$ dependence. (We neglect the small mass difference between μ_0 and $\mu_1 = \mu_2$.) In other words, the atomic states g'_α and f'_β just like the adiabatic states φ_α (hence φ'_α) are defined with reference to the rotating molecular axis.

By utilizing the completeness properties of $\{\varphi'_\alpha\}$ basis set, the state function ψ^+ of the (p^+, H) system may be written as

$$\psi^+ = \sum_t \varphi'_t(\vec{r}_0, \vec{R}_0)\Upsilon_t(\vec{R}_0) + \sum_{t'} \varphi'_{t'}(\vec{r}_0, \vec{R}_0)\Upsilon_{t'}(\vec{R}_0)\,, \tag{2.14}$$

where the t sum is over the states in which φ'_t asymptotically goes over to the atomic states g'_t centered at the target proton and the t' sum sums over the states in which $\varphi'_{t'}$ asymptotically goes over to the atomic states $f'_{t'}$ centered at the incident proton. The use of the completeness properties of atomic states $\{g_\alpha\}$ and $\{f_\alpha\}$ gives the equations

$$\sum_t g'_t(\vec{r}\,'_1)\Upsilon_t(\vec{R}_0) \equiv \Upsilon_s = \sum_t g_t(\vec{r}_1)\Psi_t(\vec{R}_1)\,, \tag{2.15a}$$

$$\sum_t f'_{t'}(\vec{r}\,'_2)\Upsilon_{t'}(\vec{R}_0) \equiv \Upsilon_r = \sum_{t'} f_{t'}(\vec{r}_2)\Psi_{t'}(\vec{R}_2)\,, \tag{2.15b}$$

for the transformations $\{\Upsilon'_t(\vec{R}_0)\} \rightarrow \{\Psi_t(\vec{R}_1)\}$ and $\{\Upsilon'_{t'}(\vec{R}_0)\} \rightarrow \{\Psi_{t'}(\vec{R}_2)\}$.

The coupled second-order differential equations obtained for $\{\Psi_\alpha\}$ take the familiar form

$$[E - W_\alpha + i\eta - K_R - \mathcal{V}_\alpha(\vec{R})]\Psi_\alpha(\vec{R}) - \sum_{\beta\neq\alpha}\mathcal{V}_{\alpha\beta}(\vec{R})\Psi_\beta(\vec{R}) = i\eta\delta_{\alpha 0}\lambda_{k_0}(\vec{R})\,, \tag{2.16}$$

where $K_{\vec{R}} = -\nabla^2_R/2M_1$, $\lambda_{k_0} = (2\pi)^{-3/2}\exp(\vec{k}_1\cdot\vec{R})$, $\vec{R}$ representing $\vec{R}_1$ or $\vec{R}_2$ is the dummy variable, and the indices α and β sum over states in both the scattering and rearrangement channels. The diagonal and coupling interactions are defined in terms of the molecular and atomic electronic states.

Let the unprimed indices refer to states in the scattering channel and primed indices to states in the rearrangement channel, then we have for the interactions[2,7]

$$\mathcal{V}_{\alpha\beta}(\vec{R}_1) = \sum_{s,t}\langle g_\alpha(\vec{r}_1)|g'_s(\vec{r}\,'_1)\mathcal{J}_{st}(\vec{R}_0)\langle g'_t(\vec{r}\,'_1)|\,e^{-i\mu\vec{\kappa}_\beta(\vec{R}_0)\cdot\vec{r}_1}g_\beta(\vec{r}_1)\rangle\rangle_{\vec{R}_0}\,e^{i\mu\vec{\kappa}_\beta(\vec{R}_1)\cdot\vec{r}_1}\rangle_{\vec{R}_1}\,, \tag{2.17a}$$

$$\mathcal{V}_{\alpha\beta'}(\vec{R}_1) = \sum_{s,t'}\langle g_\alpha(\vec{r}_1)|g'_s(\vec{r}\,'_1)\mathcal{J}_{st'}(\vec{R}_0)\langle f'_{t'}(\vec{r}\,'_2)|\,e^{i\mu\vec{\kappa}_{\beta'}(\vec{R}_0)\cdot\vec{r}_2}f_{\beta'}(\vec{r}_2)\rangle\rangle_{\vec{R}_0}\,e^{i\mu\vec{\kappa}_{\beta'}(\vec{R}_1)\cdot\vec{r}_1}\rangle_{\vec{R}_1}\,, \tag{2.17b}$$

$$\mathcal{V}_{\alpha'\beta}(\vec{R}_2) = \sum_{s't}\langle f_{\alpha'}(\vec{r}_2)|\,f'_{s'}(\vec{r}\,'_2)\mathcal{J}_{s't}(\vec{R}_0)\langle g'_t(\vec{r}\,'_1)|\,e^{-i\mu\vec{\kappa}_\beta(\vec{R}_0)\cdot\vec{r}_1}g_\beta(\vec{r}_1)\rangle\rangle_{\vec{R}_0}\,e^{-i\mu\vec{\kappa}_\beta(\vec{R}_2)\cdot\vec{r}_2}\rangle_{\vec{R}_2}\,, \tag{2.17c}$$

$$\mathcal{V}_{\alpha'\beta'}(\vec{R}_2) = \sum_{s't'}\langle f_{\alpha'}(\vec{r}_2)|f'_{s'}(\vec{r}\,'_2)\mathcal{J}_{s't'}(\vec{R}_0)\langle f'_{t'}(\vec{r}\,'_2)|\,e^{i\mu\vec{\kappa}_{\beta'}(\vec{R}_0)\cdot\vec{r}_2}f_{\beta'}(\vec{r}_2)\rangle\rangle_{\vec{R}_0}\,e^{-i\mu\vec{\kappa}_{\beta'}(\vec{R}_2)\cdot\vec{r}_2}\rangle_{\vec{R}_2}\,, \tag{2.17d}$$

with

$$\mathcal{J}_{\alpha\beta} = \Delta_{\alpha\beta} - \Delta^{(0)}_{\alpha\beta} + w_{\alpha\beta} - W'_\alpha\delta_{\alpha\beta}\,, \tag{2.18a}$$

$$\mathcal{J}_{\alpha\beta'} = \Delta_{\alpha\beta'} + w_{\alpha\beta'} - W'_\alpha\delta_{\alpha\beta'}\,, \tag{2.18b}$$

$$\mathcal{J}_{\alpha'\beta} = \Delta_{\alpha'\beta} + w_{\alpha'\beta} - W'_{\alpha'}\delta_{\alpha'\beta}\,, \tag{2.18c}$$

$$\mathcal{J}_{\alpha'\beta'} = \Delta_{\alpha'\beta'} - \Delta^{(0)}_{\alpha'\beta'} + w_{\alpha'\beta'} - W'_{\alpha'}\delta_{\alpha'\beta'}\,, \tag{2.18d}$$

where $\mu = m/(m+M)$. Now returning to the convention of Eq. (2.16) where indices α and β denote states in both scattering and rearrangement channel, then we have

$$\vec{\kappa}_\beta(\vec{R}_i) = \vec{\nabla}_{\vec{R}_0}S_\beta(\vec{R}_0)|_{\vec{R}_i}\,, \tag{2.19}$$

$$\Delta_{\alpha\beta} = (\varphi'_\alpha, [K_0, \varphi'_\beta]),\quad \Delta^{(0)}_{\alpha\beta} = \lim_{R\to\infty}\Delta_{\alpha\beta}\,, \tag{2.20}$$

$$w_{\alpha\beta} = (\varphi'_\alpha, h_0\varphi'_\beta),\quad W'_\alpha\delta_{\alpha\beta} = \lim_{R\to\infty}w_{\alpha\beta}\,, \tag{2.21}$$

where S_β are the eikonals defined by the path integrals[8]

$$S_\beta(R_0) = \int^{\vec{R}_0}[k^2_\beta - 2M_1\mathcal{V}_\beta(\vec{R}\,'_0)]^{1/2}\,ds \tag{2.22}$$

in terms of the diagonal potential $\mathcal{V}_\beta(\vec{R}_0)$.

The coupling interactions of (2.17) can be approximated by a simpler form,

$$\mathcal{V}_{\alpha\beta}(\vec{R}_1) \cong \sum_{s,t}\langle g_\alpha|\,e^{i\mu\vec{\kappa}_s\cdot\vec{r}_1}|g'_s\rangle_{\vec{R}_1}\mathcal{J}_{st}(\vec{R}_1)\langle g'_t|\,e^{-i\mu\vec{\kappa}_t\cdot\vec{r}_1}|g_\beta\rangle_{\vec{R}_1}\,, \tag{2.23a}$$

$$\mathcal{V}_{\alpha\beta'}(\vec{R}_1) \cong \sum_{st'}\langle g_\alpha|\,e^{i\mu\vec{\kappa}_s\cdot\vec{r}_1}|\,g'_s\rangle_{\vec{R}_1}\mathcal{J}_{st'}(\vec{R}_1)\langle f'_{t'}|\,e^{i\mu\vec{\kappa}_{t'}\cdot\vec{r}_2}|f_{\beta'}\rangle_{\vec{R}_1}\,, \tag{2.23b}$$

$$\mathcal{V}_{\alpha'\beta}(\vec{R}_2) \cong \sum_{s't}\langle f_{\alpha'}|\,e^{-i\mu\vec{\kappa}_{s'}\cdot\vec{r}_2}|f'_{s'}\rangle_{\vec{R}_2}\mathcal{J}_{s't}(\vec{R}_2)\langle g'_t|\,e^{-i\mu\vec{\kappa}_t\cdot\vec{r}_1}|g_\beta\rangle_{\vec{R}_2}\,, \tag{2.23c}$$

$$\mathcal{V}_{\alpha'\beta'}(\vec{R}_2) \cong \sum_{s't'}\langle f_{\alpha'}|\,e^{-i\mu\vec{\kappa}_{s'}\cdot\vec{r}_2}|f'_{s'}\rangle_{\vec{R}_2}\mathcal{J}_{s't'}(\vec{R}_2)\langle f'_{t'}|\,e^{i\mu\vec{\kappa}_{t'}\cdot\vec{r}_2}|\,f_{\beta'}\rangle_{\vec{R}_2}\,. \tag{2.23d}$$

The separation of the translational contribution from the nonadiabatic interaction involving molecular states greatly simplifies the evaluation of these coupling interactions.

The form of Eqs. (2.17) and (2.23) allows a simple physical interpretation of the interactions to be given. Through the translational factors the asymptotic atomic state expressed in a space-fixed coordinate is transformed into a set of atomic states expressed in the rotating coordinates. These rotating atomic states are then merged into molecular states. Through the nonadiabatic interactions, transitions between the molecular states can take place both on their way into the united-atom states and on their way out to the separated-atom states. These final atomic states are then transferred into space-fixed atomic states through the translational factors.

III. EVALUATION OF THE NONADIABATIC INTERACTIONS

A. Reduction in eikonal approximation

The evaluation of the nonadiabatic interactions $\Delta_{\alpha\beta}$ and $\Delta_{\alpha\beta}^{(0)}$ are simplified by the eikonal and straight-line approximations. To exhibit the Hermitian form of the interaction, the nonadiabatic interaction [Eq. (2.20)] can be written as

$$\begin{aligned}\Delta_{\alpha\beta}= -(1/2M_0)[&\vec{\nabla}^{\dagger}_{\vec{R}_0}\cdot(\varphi'_\alpha, \vec{\nabla}^{\dagger}_{\vec{R}_0}\varphi'_\beta)_{\vec{R}_0} \\ &+(\varphi'_\alpha, \vec{\nabla}_{\vec{R}_0}\varphi'_\beta)_{\vec{R}_0}\cdot\vec{\nabla}_{\vec{R}_0}] \\ -(1/4M_0)[&(\varphi'_\alpha, \vec{\nabla}^{2\dagger}_{\vec{R}_0}\varphi'_\beta)+(\varphi'_\alpha, \vec{\nabla}^{2}_{\vec{R}_0}\varphi'_\beta)]\,.\end{aligned} \tag{3.1}$$

If the gradient operators are allowed to act on the nuclear wave functions $\Psi_\alpha(\vec{R})$ and $\Psi_\beta(\vec{R})$ in the eikonal approximation, the nonadiabatic interactions take the form

$$\Delta_{\alpha\beta}= -\frac{1}{M_0}i\left(\frac{\vec{\kappa}^*_\alpha+\vec{\kappa}_\beta}{2}\right)\cdot(\varphi'_\alpha, \vec{\nabla}_{\vec{R}_0}\varphi'_\beta)_{\vec{R}_0}\,, \tag{3.2}$$

where the $\vec{\nabla}^2_{\vec{R}_0}$ terms in (3.1) are neglected. In the straight-line approximation with $\hat{z}$ taken to be the incident direction, Eq. (3.2) reduces to the form

$$\Delta_{\alpha\beta}= -\frac{1}{M_0}i\left(\frac{\kappa^*_\alpha+\kappa_\beta}{2}\right)\times\left[\frac{z}{R}\left(\varphi'_\alpha, \frac{\partial}{\partial R_0}\varphi'_\beta\right)-i\frac{B}{R_0^2}(\varphi'_\alpha, J_{y_0}\varphi'_\beta)\right] \tag{3.3}$$

with

$$iJ_{y_0}=\cos\phi_0\frac{\partial}{\partial\theta_0}-\cot\theta_0\sin\phi_0\frac{\partial}{\partial\phi_0}\,, \tag{3.4}$$

where B is the impact parameter and we have made use of the relation $\vec{r}_0=(x_0y_0z_0)=(r_0\theta_0\phi_0)$ for the electron. The first term [on the right-hand side of (3.3)] which gives rise to the radial coupling is an odd function of z and the second term which gives rise to the rotational coupling is an even function of z. A similar expression for $\Delta_{\alpha\beta}^{(0)}$ can be obtained in terms of the atomic states.

The evaluation of the nonadiabatic interactions is carried out in three steps: (1) generation of the adiabatic H_2^+ electronic states, (2) numerical calculation of the matrix elements $\Delta_{\alpha\beta}$, and (3) analytic determination of $\Delta_{\alpha\beta}^{(0)}$.

B. Adiabatic H_2^+ electronic states

The adiabatic H_2^+ electron wave functions can, in principle, be generated exactly, since the Hamiltonian [Eq. (2.10c)] is separable in confocal elliptic (prolate spheroidal) coordinates (ξ, η, ϕ):

$$\xi=(r_1+r_2)/R_0, \quad \eta=(r_1-r_2)/R_0\,. \tag{3.5}$$

This leads to three ordinary uncoupled differential equations:

$$\left(\frac{d^2}{d\phi^2}-m^2\right)\Phi=0\,, \tag{3.6a}$$

$$\left(\frac{d}{d\eta}(1-\eta^2)\frac{d}{d\eta}-A'-p^2(1-\eta^2)-\frac{m^2}{1-\eta^2}\right)\mathcal{H}=0\,, \tag{3.6b}$$

$$\left(\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}+A'-p^2(\xi^2-1)-\frac{m^2}{\xi^2-1}+2R_0\xi\right)\Xi=0\,, \tag{3.6c}$$

with

$$p^2=-R_0^2w/2, \quad A'=A-p^2\,, \tag{3.7}$$

where A and m are separation constants, w is the electronic energy of H_2^+ molecule, and R_0 is the internuclear separation.

The wave functions of these equations have been published by Bates *et al.*[9] for internuclear separations $R_0=0$ to $R_0=9.0$ a.u. We have extended the solution to $R_0=150$ a.u.[10] In Fig. 2, the corresponding total electronic energies of these H_2^+ adiabatic electronic states are shown as functions of the internuclear separation.

C. Calculation of $\Delta_{\alpha\beta}$

To evaluate $\Delta_{\alpha\beta}$, it is convenient to express the radial and rotational coupling matrix elements in terms of the prolate spheroidal coordinates. We have (in terms of adiabatic electronic states)

$$\left(\varphi_\alpha, \frac{\partial}{\partial R_0}\varphi_\beta\right)=-\frac{4}{R_0^2}\frac{1}{\omega_\beta-\omega_\alpha}\left(\varphi_\alpha, \frac{\xi}{\xi^2-\eta^2}\varphi_\beta\right)-\frac{1}{R_0}\left(\varphi_\alpha, \frac{1}{\xi^2-\eta^2}\xi(\xi^2-1)\frac{\partial}{\partial\xi}\varphi_\beta\right)-\frac{1}{R_0}\left(\varphi_\alpha, \frac{1}{\xi^2-\eta^2}\eta(1-\eta^2)\frac{\partial}{\partial\eta}\varphi_\beta\right), \tag{3.8}$$

$$(\varphi_\alpha, iJ_{y_0}\varphi_\beta)=\left(\varphi_\alpha, \cos\phi\frac{[(\xi^2-1)(1-\eta^2)]^{1/2}}{\xi^2-\eta^2}\left(\eta\frac{\partial}{\partial\xi}-\xi\frac{\partial}{\partial\eta}\right)\varphi_\beta\right)-\left(\varphi_\alpha, \sin\phi\frac{\xi\eta}{[(\xi^2-1)(1-\eta^2)]^{1/2}}\frac{\partial}{\partial\phi}\varphi_\beta\right), \tag{3.9}$$

where the radial matrix elements (3.8) satisfy the selection rule $\Delta m = m_\alpha - m_\beta = 0$ and the rotational coupling matrix elements (3.9) satisfy the selection rule $\Delta m = m_\alpha - m_\beta = \pm 1$.

It is appropriate to recall that the states φ'_α are linear combinations of the adiabatic electronic states φ_α. We have, for example,

$$\varphi'_{1s_A}=(1/\sqrt{2})(\varphi_{1s\,\sigma_g}+\varphi_{2p\,\sigma_u}), \tag{3.10a}$$

$$\varphi'_{1s_B}=(1/\sqrt{2})(\varphi_{1s\,\sigma_g}-\varphi_{2p\,\sigma_u}), \tag{3.10b}$$

$$(\varphi'_{2s})_1=\tfrac{1}{2}(\varphi_{2s\,\sigma_g}+\varphi_{3d\,\sigma_g}+\varphi_{3p\,\sigma_u}+\varphi_{4f\,\sigma_u}), \tag{3.11a}$$

$$(\varphi'_{2s})_2=\tfrac{1}{2}(\varphi_{2s\,\sigma_g}+\varphi_{3d\,\sigma_g}-\varphi_{3p\,\sigma_u}-\varphi_{4f\,\sigma_u}), \tag{3.11b}$$

$$(\varphi'_{2p_0})_1=\tfrac{1}{2}(\varphi_{3d\,\sigma_g}-\varphi_{2s\,\sigma_g}+\varphi_{4f\,\sigma_u}-\varphi_{3p\,\sigma_u}), \tag{3.12a}$$

$$(\varphi'_{2p_0})_2=\tfrac{1}{2}(\varphi_{3d\,\sigma_g}-\varphi_{2s\,\sigma_g}-\varphi_{4f\,\sigma_u}+\varphi_{3p\,\sigma_u}), \tag{3.12b}$$

$$(\varphi'_{2p_{\cos\phi}})_1=(1/\sqrt{2})(\varphi_{3d\,\pi_g}+\varphi_{2p\,\pi_u}), \tag{3.13a}$$

$$(\varphi'_{2p_{\cos\phi}})_2=(1/\sqrt{2})(\varphi_{3d\,\pi_g}-\varphi_{2p\,\pi_u}), \tag{3.13b}$$

where the subscripts 1 and 2 denote the asymptotic atomic centers [see Eqs. (2.13)], for example,

$$(\varphi_{2p_0})_1 \to g'_{2p_0}(\vec{r}'_1)=(32\pi)^{-1/2}r_1\cos\theta'_1\,e^{-r_1/2},$$

$$(\varphi_{2p_{\cos\phi}})_2 \to f'_{2p_{\cos\phi}}(\vec{r}'_2)=(32\pi)^{-1/2}r_2\cos\theta'_2\cos\varphi_2\,e^{-r_2/2}.$$

These combinations are based on the coordinates of Fig. 3 in which the z axes of the electron centered at the two protons are pointing in the opposite direction along the rotating molecular axis. Thus in general the radial coupling matrix elements $(\varphi'_\alpha, (\partial/\partial R_0)\varphi'_\beta)$ and the rotational coupling matrix elements $(\varphi'_\alpha, iJ_{y_0}\varphi'_\beta)$ can be expressed as a linear combination of those matrix elements of (3.8) and (3.9).

The nonadiabatic electronic matrix elements between the adiabatic H_2^+ electronic state [Eqs. (3.8) and (3.9)] which asymptotically go to the $n=1$ or $n=2$ atomic states have been calculated for internuclear separations $R_0=0$ to $R_0=150$ a.u.[10] In Fig. 4, the nonadiabatic radial couplings (multiplied by a factor of R_0/z) are given as functions of internuclear separation R_0. It is seen that some of the radial couplings approach constant values. A comparison of the nonadiabatic rotational couplings (multiplied by a factor of R_0^2/B) is given in Fig. 5. It is apparent that the nonadiabatic rotational couplings have spurious long-range interactions. These long-range interactions in both the radial and rotational coupling are coming from our choice of the $(\vec{r}_0, \vec{R}_0)$ coordinates for the adiabatic H_2^+ electronic states.[2,7] To remove these long-range interactions we need to evaluate $\Delta^{(0)}_{\alpha\beta}$. Our results agree with those calculated by Rosenthal.[11]

D. Analytic determination of $\Delta^{(0)}_{\alpha\beta}$

By definition [Eq. (2.20)], $\Delta^{(0)}_{\alpha\beta}$ are the asymptotic forms of the nonadiabatic interaction $\Delta_{\alpha\beta}$. They are needed only between atomic states which are centered either at the target proton or at the inci-

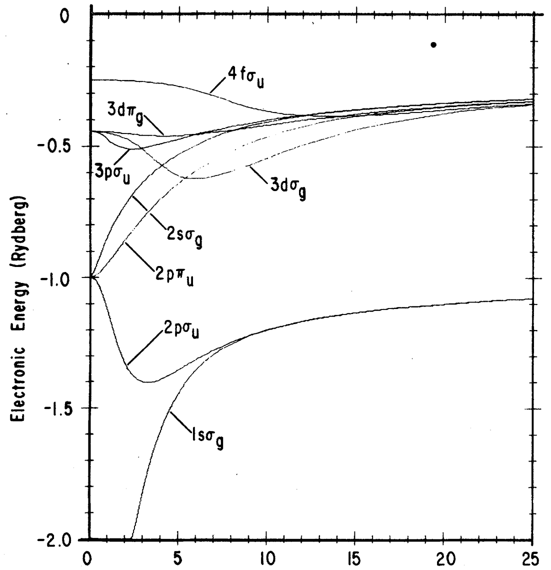

FIG. 2. Electronic energies as a function of internuclear separation of the adiabatic molecular states which go to $n=1$ or $n=2$ atomic states, asymptotically.

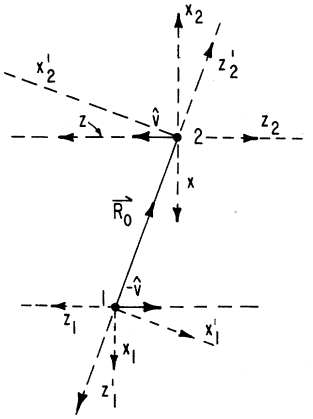

FIG. 3. Space-fixed and rotating coordinate systems for the electron centered at the two protons with the y axes pointing upwards from the x-z planes.

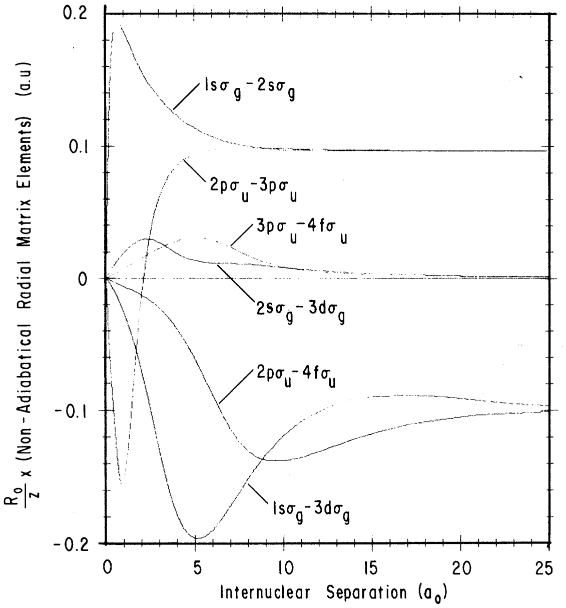

FIG. 4. Nonadiabatic radial matrix elements $\hat{z}\cdot(\varphi_\alpha,\vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0}R_0/z=(\varphi_\alpha,(\partial/\partial R_0)\varphi_\beta)_{\vec{R}_0}$, $\Delta m=0$, as a function of internuclear separation between states which go to $n=1$ or $n=2$ atomic states, asymptotically.

dent proton [see Eqs. (2.18a) and (2.18d)]. From the symmetry consideration (see Fig. 3) we have

$$(g'_\alpha,\vec{\nabla}_{\vec{R}_0}g'_\beta)=(f'_\alpha,\vec{\nabla}_{\vec{R}_0}f'_\beta)\,. \tag{3.14}$$

Thus, we need only evaluate one set of these matrix elements. The matrix elements (3.14) are expressed in terms of atomic states which are defined, just as the adiabatic electronic states, with reference to the rotating molecular axis.

With the exact atomic states available, the matrix elements are evaluated in closed forms. We have

$$\Delta^{(0)}_{1s,2s}=0\,,\quad \Delta^{(0)}_{1s2p_0}=+iv\frac{z}{R_0}\frac{8\sqrt{2}}{81}\,,$$
$$\Delta^{(0)}_{1s2p_{\cos\phi}}=-iv\frac{B}{R_0}\frac{8\sqrt{2}}{81}\,,\quad \Delta^{(0)}_{2s2p_0}=0,$$
$$\Delta^{(0)}_{2s2p_{\cos\phi}}=0,\quad \Delta^{(0)}_{2p_02p_{\cos\phi}}=-ivB/R_0^2\,, \tag{3.15}$$

where v is the magnitude of the relative colliding velocity.

According to the linear relations given by (3.10) to (3.13) the asymptote forms of $(\varphi_\alpha,(\partial/\partial R_0)\varphi_\beta)$ and $(\varphi_\alpha,iJ_{y_0}\varphi_\beta)$ are linear combinations of $\Delta^{(0)}_{\alpha\beta}$. By utilizing these expressions for $\Delta^{(0)}_{\alpha\beta}$, the long-range interaction in Figs. 4 and 5 can be removed. The results are shown in Figs. 6 and 7. It is clear that all the long-range interactions are removed.

We emphasize that the complete removal of the spurious long-range interaction by the subtraction of $\Delta^{(0)}_{\alpha\beta}$ from $\Delta_{\alpha\beta}$ is a consequence of two fac-

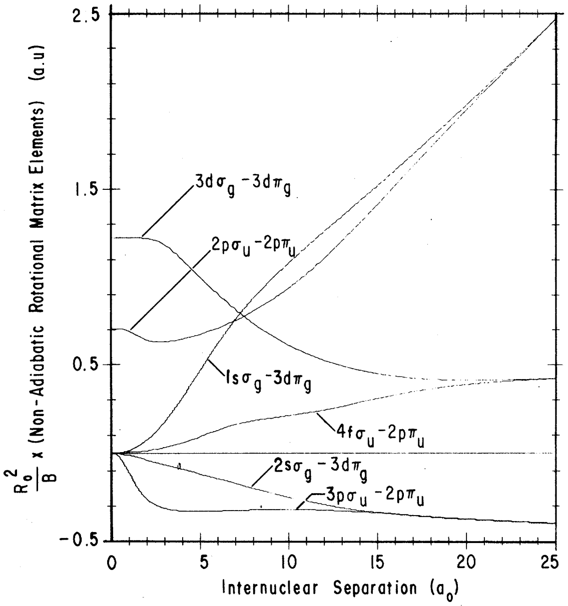

FIG. 5. Nonadiabatic rotational matrix elements $\hat{z}\cdot(\varphi_\alpha,\vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0}R_0^2/B=-(\varphi_\alpha,iJ_{y_0}\varphi_\beta)_{\vec{R}_0}$, $\Delta m=\pm1$ as a function of internuclear separation between states which go to $n=1$ or $n=2$ atomic states, asymptotically.

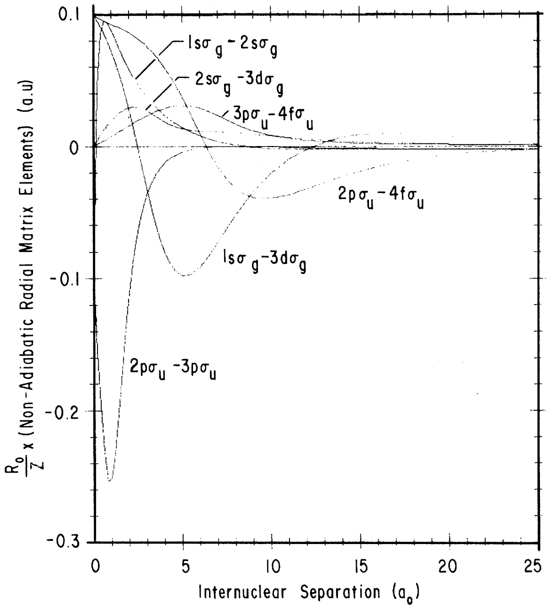

FIG. 6. Nonadiabatic radial matrix elements minus their asymptotic limits $(R_0/z)[\hat{z}\cdot(\varphi_\alpha,\vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0}-\hat{z}\cdot(f'_\alpha,\vec{\nabla}_{\vec{R}_0}f'_\beta)_{\vec{R}_0}]$, as a function of internuclear separation between states which go to $n=1$ or $n=2$ atomic states, asymptotically.

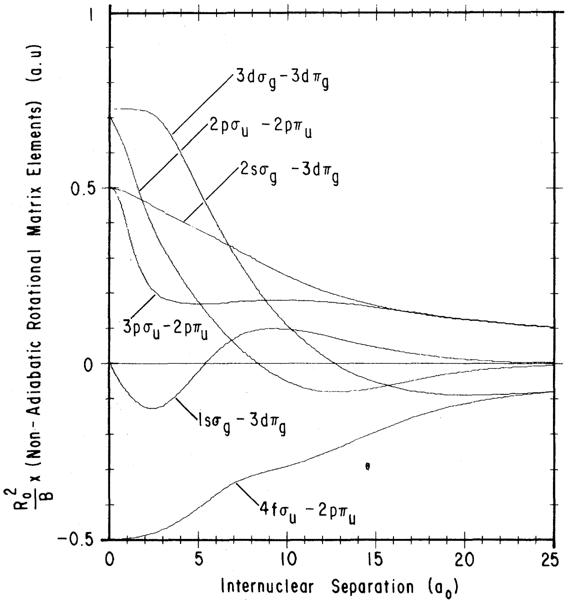

FIG. 7. Nonadiabatic rotational matrix elements minus their asymptotic limits $(R_0^2/z)[\hat{z}\cdot(\varphi_\alpha,\vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0}-\hat{z}\circ(f'_\alpha,\vec{\nabla}_{\vec{R}_0}f'_\beta)_{\vec{R}_0}]$, as a function of internuclear separation between states which go to $n=1$ or $n=2$ atomic states, asymptotically.

tors: (1) the transformation of kinetic-energy operator in the $(\vec{R}_0,\vec{r}_0)$ coordinate system to the proper coordinate systems $(\vec{R}_1,\vec{r}_1)$ and $(\vec{R}_2,\vec{r}_2)$ for scattering and rearrangement channels, respectively, and (2) the use of space-fixed atomic basis sets $\{g_\alpha(\vec{r}_1)\}$ and $\{f_\alpha(\vec{r}_2)\}$. If we choose not to use these space-fixed atomic basis states and use instead the atomic basis sets $\{g'_\alpha(\vec{r}'_1)\}$ and $\{f'_\alpha(\vec{r}'_2)\}$ defined with reference to the rotating molecular axis, then not all the long-range interactions can be removed. This is because the rotating atomic states do not in general commute with the nuclear kinetic-energy operator and give rise to terms which cancel $\Delta^{(0)}_{\alpha\beta}$ obtained from coordinate transformation of the kinetic energy operator.

In Fig. 8, the rotational coupling interactions obtained by the use of the rotating atomic basis states are shown. From the comparison with Fig. 7, it is apparent that long-range interactions are present in $(\varphi_{3d\sigma_g}, iJ_{y_0}\varphi_{3d\pi_g})$, $(\varphi_{4f\sigma_u}, iJ_{y_0}\varphi_{2p\pi_u})$, $(\varphi_{2s\sigma_g}, iJ_{y_0}\varphi_{3d\pi_g})$, and $(\varphi_{3p\sigma_u}, iJ_{y_0}\varphi_{2p\pi_u})$ matrix elements. These long-range interactions are generated by the asymptotic rotational coupling between the g'_{2p_0} and $g'_{2p_{\cos\phi}}$ (or f'_{2p_0} and $f'_{2p_{\cos\phi}}$) atomic states. We have

$$(g'_{2p_0}\, iJ_{y_0} g'_{2p_{\cos\phi}})=1\,.$$

Physically it is expected that all states are uncoupled asymptotically. This long-range interaction is due entirely to the choice of the basis set and can be removed only by the use of space-fixed atomic basis states. It should, however, be noted that due to the $2s$ and $2p_0$ degeneracy of the hydrogen atom, a dipole interaction ($\sim R^{-2}$) is generated by the interaction with the proton at large distances. This long-range dipole interaction is not coming from the choice of coordinate systems and is accounted for by the molecular electronic states, $2s\sigma_g$, $3d\sigma_g$, $2p\sigma_u$, and $4f\sigma_u$ which go to linear combinations of the $2s$ and $2p_0$ atomic states.

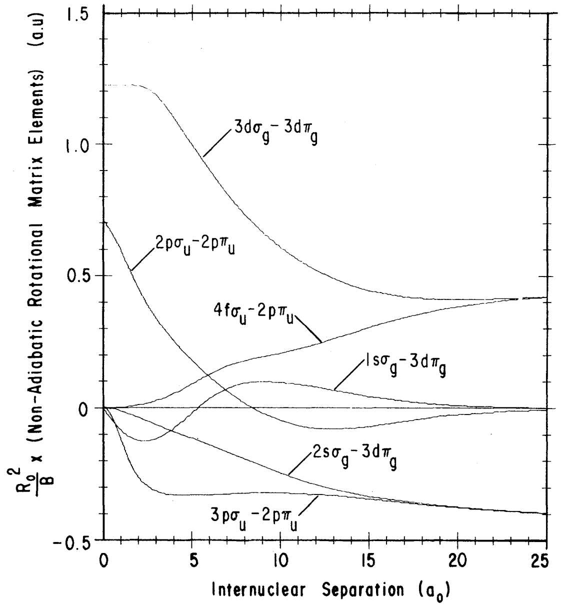

FIG. 8. Internuclear-separation dependence of the nonadiabatic rotational matrix elements minus their asymptotic limits for the case with rotating atomic basis, $(R_0^2/z)[\hat{z}\cdot(\varphi_\alpha,\vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0}-\hat{z}\cdot(f'_\alpha,\vec{\nabla}_{\vec{R}_0}f'_\beta)_{\vec{R}_0}+(f'_\alpha(d/dz)f'_\beta)]$, where the last term [see Eq. (A6) in the Appendix], comes from the fact that the rotating atomic states do not commute with the kinetic-energy operator K_2 [see Eq. (2.8b)], between states which go to $n=1$ or $n=2$ atomic states, asymptotically.

IV. TRANSLATIONAL-FACTOR CONTRIBUTION

A. Calculation of translational matrix elements

The translational matrix elements [see Eqs. (2.23a)–(2.23d)] are defined in terms of atomic states of mixed bases centered on one of the protons. From Fig. 3, it is seen that

$$\langle g_\alpha(\vec{r}_1)|e^{i\vec{v}_\beta\cdot\vec{r}_1/2}|g'_\beta(\vec{r}'_1)\rangle=\langle f_\alpha(\vec{r}_2)|e^{-i\vec{v}_\beta\cdot\vec{r}_2/2}|f'_\beta(\vec{r}'_2)\rangle\,, \tag{4.1a}$$

$$\langle g'_\alpha(\vec{r}'_1)|e^{-i\vec{v}_\alpha\cdot\vec{r}_1/2}|g_\beta(\vec{r}_1)\rangle=\langle f'_\alpha(\vec{r}'_2)|e^{i\vec{v}_\alpha\cdot\vec{r}_2/2}|f_\beta(\vec{r}_2)\rangle\,. \tag{4.1b}$$

With these relations we need to evaluate only one set of the matrix elements.

The evaluation of these matrix elements in the mixed bases can be simplified by the use of the completeness properties of $\{f_\alpha(\vec{r}_2)\}$. We have

$$\tau^{(\pm)}_{\alpha\beta} \equiv \langle f_\alpha(\vec{r}_2) | e^{\pm i\vec{v}_\beta \cdot \vec{r}_2/2} | f'_\beta(\vec{r}'_2)\rangle = \sum_\gamma \langle f_\alpha(\vec{r}_2) | e^{\pm i\vec{v}_\beta \cdot \vec{r}_2/2} | f_\gamma(\vec{r}_2)\rangle \langle f_\gamma(\vec{r}_2) | f'_\beta(\vec{r}'_2)\rangle \,. \tag{4.2}$$

The overlap matrix elements $\langle f_\gamma(\vec{r}_2) | f'_\beta(\vec{r}'_2)\rangle$ can be nonzero only between magnetic substates. This is evident since the space-fixed and rotating atomic states are related by a rotation. We have, for $n=1$ and $n=2$,

$$f_{1s}(\vec{r}_2) = f'_{1s}(\vec{r}'_2), \quad f_{2s}(\vec{r}_2) = f'_{2s}(\vec{r}'_2)\,, \tag{4.3a}$$

$$f_{2p\,0}(\vec{r}_2) = -(z/R_0) f'_{2p\,0}(\vec{r}'_2) - (B/R_0) f'_{2p_{\cos\phi}}(\vec{r}'_2)\,, \tag{4.3b}$$

$$f_{2p_{\cos\phi}}(\vec{r}_2) = -(z/R_0) f'_{2p_{\cos\phi}}(\vec{r}'_2) + (B/R_0) f'_{2p\,0}(\vec{r}'_2)\,. \tag{4.3c}$$

The translational matrix elements $\tau^{(\pm)}_{\alpha\beta}$ can be evaluated in closed form. We have, for example,

$$\tau^{(\pm)}_{1s,\,1s} = \frac{1}{[1+(v_1/4)^2]^2}\,, \quad \tau^{(\pm)}_{2s,\,2s} = \frac{1-3(v_2/2)^2+2(v_2/2)^4}{[1+(v_2/2)^2]^3}\,, \tag{4.4a}$$

$$\tau^{(\pm)}_{1s,\,2s} = \frac{2^6\sqrt{2}}{3^4} \frac{(v_2/3)^2}{[1+(v_2/3)^2]^3} = \tau^{(\pm)}_{2s,\,1s}\,, \tag{4.4b}$$

$$\tau^{(\pm)}_{1s,\,2p\,0} = \pm i(z/R_0)A(v_2), \quad \tau^{(\pm)}_{1s,\,2p_{\cos\phi}} = \mp i(B/R_0)A(v_2)\,, \tag{4.4c}$$

$$\tau^{(\pm)}_{2s,\,2p\,0} = \mp i(z/R_0)B(v_2), \quad \tau^{(\pm)}_{2s,\,2p_{\cos\phi}} = \pm i(B/R_0)B(v_2)\,, \tag{4.4d}$$

$$\tau^{(\pm)}_{2p\,0,\,1s} = \mp iA(v_2), \quad \tau^{(\pm)}_{2p\,0,\,2s} = \pm iB(v_2)\,, \tag{4.4e}$$

$$\tau^{(\pm)}_{2p\,0,\,2p\,0} = -(z/R)C(v_2), \quad \tau^{(\pm)}_{2p\,0,\,2p_{\cos\phi}} = +(B/R_0)C(v_2)\,, \tag{4.4f}$$

$$\tau^{(\pm)}_{2p_{\cos\phi},\,1s} = \tau^{(\pm)}_{2p_{\cos\phi},\,2s} = 0\,, \tag{4.4g}$$

$$\tau^{(\pm)}_{2p_{\cos\phi},\,2p\,0} = -(B/R_0)D(v_2), \quad \tau^{(\pm)}_{2p_{\cos\phi},\,2p_{\cos\phi}} = -(z/R_0)D(v_2)\,, \tag{4.4h}$$

where

$$A(v) = \frac{2^6\sqrt{2}}{3^5} \frac{v}{[1+(v/3)^2]^3}, \quad B(v) = \tfrac{3}{2}v \frac{1-(v/2)^2}{[1+(v/2)^2]^4}\,,$$

$$C(v) = \frac{1-5(v/2)^2}{[1+(v/2)^2]^4}, \quad D(v) = \frac{1}{[1+(v/2)^2]^3}\,.$$

The velocity dependence of the translational matrix elements is given in Fig. 9. The effect of these translational factors may be visualized through their effect on the $2p\sigma_u$-$2p\pi_u$ nonadiabatic interaction which dominates the $1s \rightarrow 2p_{\cos\phi}$ excitation process. Let us consider the coupling term

$$\tau^{(\pm)}_{\alpha 2p_{\cos\phi}} \mathcal{J}_{2p_{\cos\phi},\,1s} \tau^{(\mp)}_{1s\beta}\,.$$

At low velocities where the coupling matrix elements $\tau^{(\pm)}_{1s,\,1s}$ are essential unity, the $1s \rightarrow 2p_{\cos\phi}$ excitation proceeds with the help of the $\tau_{2p_{\cos\phi}2p_{\cos\phi}}$ matrix elements without much loss of its amplitude. As the nuclear velocity increases, the other $\tau^{(\pm)}_{\alpha 2p_{\cos\phi}}$ and $\tau^{(\mp)}_{1s\beta}$ matrix elements become appreciable (see curves 5 to 8 in Fig. 9) causing a redistribution of the amplitude into other channels.

B. Space-fixed and rotating atomic bases

As was pointed out in Sec. III D, the appropriate coordinate transformation of the kinetic-energy operator alone does not remove all the long-range interactions. Some of the asymptotic rotational coupling can be removed only if a space-fixed atomic basis is used. Calculations for the (p^+, H) system reported in the literature are carried out

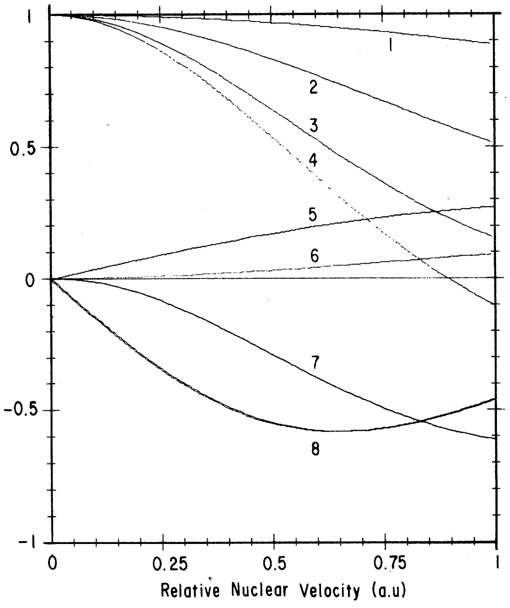

FIG. 9. Velocity (a.u.) dependence of the translational matrix elements $\tau_{\alpha\beta} = \langle f_\alpha(\vec{r}_2) | e^{i\vec{v}\cdot\vec{r}_2/2} | f'_\beta(\vec{r}'_2)\rangle$: Curve 1, $\tau_{1s,\,1s}$; curve 2, $D(v)$; curve 3, $\tau_{2s,\,2s}$; curve 4, $C(v)$; curve 5, $A(v)$; curve 6, $\tau_{1s,\,2s} = \tau_{2s,\,1s}$; curve 8, $-\boldsymbol{B}(v)$. $A(v)$, $B(v)$, $C(v)$, and $D(v)$ are defined following Eqs. (4.4) for the translational matrix elements $\tau^{(\pm)}_{\alpha\beta}$.

in states which are expressed in coordinate systems rotating with the molecular axis. Here we examine the effect of the rotating atomic states in the translational contributions. In the Appendix, the transformation of the coupled equations from the space-fixed atomic basis to the rotating atomic basis is examined.

If the rotating atomic basis is used, we have

$$T_{\alpha\beta}^{(\pm)\prime}=\sum_{\gamma\gamma'}\langle f'_\alpha(\vec{r}'_2)|f_\gamma(\vec{r}_2)\rangle\langle f_\gamma(\vec{r}_2)|e^{\pm i\vec{v}_\beta\cdot\vec{r}_2/2}|f_\gamma(\vec{r}_2)\rangle \times\langle f_\gamma(\vec{r}_2)|f'_\beta(\vec{r}'_2)\rangle, \tag{4.5}$$

which can be evaluated using the same techniques. The results are not changed for Eqs. (4.4a) to (4.4d). For the rest of the matrix elements, we have

$$T_{2p_0 1s}^{(\pm)\prime}=T_{1s\,2p_0}^{(\pm)},\quad T_{2p_0 2s}^{(\pm)\prime}=T_{2s\,2p_0}^{(\pm)}, \tag{4.6a}$$

$$T_{2p_{\cos\phi},\,1s}^{(\pm)\prime}=T_{1s,\,2p_{\cos\phi}}^{(\pm)},\quad T_{2p_{\cos\phi},\,2s}^{(\pm)\prime}=T_{2s,\,2p_{\cos\phi}}^{(\pm)}, \tag{4.6b}$$

$$T_{2p_0,\,2p_0}^{(\pm)\prime}=\frac{1-(5-6B^2/R_0^2)(v_2/2)^2}{[1+(v_2/2)^2]^4}, \tag{4.6c}$$

$$T_{2p_0,\,2p_{\cos\phi}}^{(\pm)\prime}=T_{2p_{\cos\phi},\,2p_0}^{(\pm)\prime}=\frac{zB}{R_0^2}\frac{\frac{3}{2}{v_2}^2}{[1+(v_2/2)^2]^4}, \tag{4.6d}$$

$$T_{2p_{\cos\phi},\,2p_{\cos\phi}}^{(\pm)\prime}=\frac{1-(5-6z^2/R_0^2)(v_2/2)^2}{[1+(v_2/2)^2]^4}. \tag{4.6e}$$

In this rotating atomic basis, all the translational factors approach either zero or unity in the $v\rightarrow 0$ limit due to the orthonormal properties of the atomic states. Its effect can be clearly seen in examining the residual translational contributions.

C. Residual translation contributions

The effect of the translational factors on the interactions $\mathcal{V}_{\alpha\beta}$ is examined in Sec. IV A. It is seen that through the translational matrix elements, the interaction $\mathcal{I}_{\alpha\beta}$ is redistributed according to the collision velocity to give rise to the interaction $\mathcal{V}_{\alpha\beta}$. This effect of translational factor increases with velocity. What happens to this effect if the velocity is considerably decreased? At what velocity can the translational effects be neglected? To answer these questions, we examine here the effect of the translational factors in the zero-velocity limit.

In the $v\rightarrow 0$ limit, the translational factors affect the coupling interactions $\mathcal{V}_{\alpha\beta}$ (1) through the nonorthogonality of the mixed atomic bases and (2) by supplying the velocity dependence to the potential portion of $\mathcal{I}_{\alpha\beta}$ [see Eqs. (2.18)] which is velocity independent.

The nonorthogonal effect can be most easily examined for the nonadiabatic portion of $\mathcal{I}_{\alpha\beta}$. By replacing the translational factors with unity in the $v\rightarrow 0$ limit, we have

$$\sum_{s't'}\langle f_\alpha(\vec{r}_2)|f'_{s'}(\vec{r}'_2)\rangle(\Delta_{s't'}-\Delta_{s't'}^{(0)})\langle f'_{t'}(\vec{r}'_2)|f_\beta(\vec{r}_2)\rangle\equiv\mathcal{V}_{\alpha\beta}^{(1)}. \tag{4.7}$$

With the help of the transformation relations between the space-fixed and rotating atomic states given by (4.3), we obtain from (4.7), for example

$$\mathcal{V}_{1s\,2p_0}^{(1)}=-(z/R_0)(\Delta_{1s\,2p_0}-\Delta_{1s\,2p_0}^{(0)}) +(B/R_0)(\Delta_{1s,\,2p_{\cos\phi}}-\Delta_{1s,\,2p_{\cos\phi}}^{(0)}).$$

Thus the nonorthogonality retains the mixing of states which are rotationally coupled asymptotically. Of course this mixing is lost if the rotating atomic basis is used.

The nonadiabatic interactions $\Delta_{\alpha\beta}$ and $\Delta_{\alpha\beta}^{(0)}$ are first-order in v [see Eqs. (3.3)]. To examine the $v\rightarrow 0$ limit of $\mathcal{V}_{\alpha\beta}$, we need to retain the potential portions of the $\mathcal{I}_{\alpha\beta}$ [i.e. $w_{\alpha\beta}-W_\alpha\delta_{\alpha\beta}$, see Eqs. (2.18)] terms to first order in v coming from the translational factors. This $v\rightarrow 0$ contribution of the translational factors can be most clearly seen in the rotating atomic basis, without including the contribution coming from the nonorthogonality of the atomic basis states. In Figs. 10 and 11 the $v\rightarrow 0$ limits of $\mathcal{V}_{\alpha\beta}$ between the $H_2{}^+$ adiabatic states

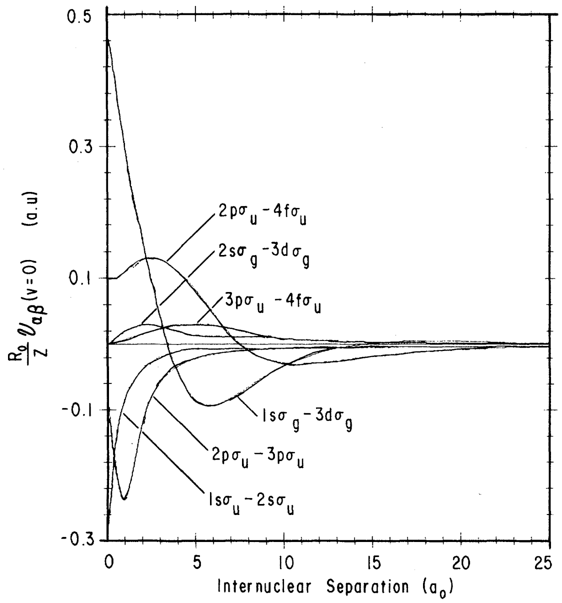

FIG. 10. Internuclear-separation dependence of the interaction $\mathcal{V}_{\alpha\beta}$ multiplied by a factor of R_0/z in the $v=0$ limit (residual translational effect) between states which are radially coupled.

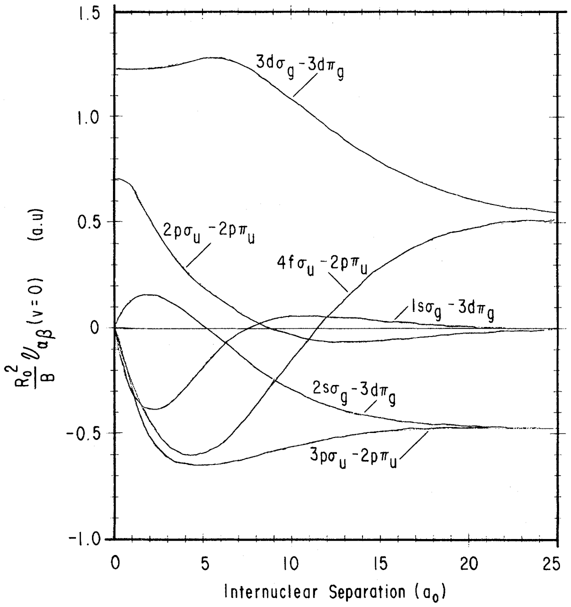

FIG. 11. Internuclear-separation dependence of the interaction $\mathcal{V}'_{\alpha\beta}$ multiplied by a factor of R_0^2/B in the $v=0$ limit (residual translational effect) between states which are rotationally coupled.

are shown for the radial couplings and rotational couplings, respectively. The residual translational effect can be seen by comparing Figs. 10 and 11 with Figs. 6 and 8. The results presented in Figs. 10 and 11 are obtained using the rotating atomic basis which affects the rotation coupling.

V. DISCUSSION AND CONCLUSIONS

With the interactions calculated, we are now in a position to examine their general features in connection with the current conceptual model for electronic transitions in atomic collisions. One of the basic questions of current interest concerns the proper molecular electronic basis. We shall discuss the adiabatic-diabatic question in connection with the noncrossing rule and dynamic correlations between the separated and united atomic states. The validity of the "coupling hypothesis" which is a basic ingredient of the Landau-Zener model for electronic transitions in slow-atom collisions is examined in terms of the calculated interactions. The characteristic features of the radial and rotational couplings are then discussed in a phase-interference model.

A. Noncrossing rules and the adiabatic-diabatic questions

By examining the irreducible matrix for states of a given symmetry, Wigner and von Neumann have shown that the crossing of states of the same symmetry requires the specification of two (three) physical parameters of the real (complex) Hamiltonian.[12] The adiabatic electronic Hamiltonian of a diatomic colliding system has only one physical parameter, namely the internuclear separation R_0; consequently the adiabatic electronic states of the same symmetry cannot cross. This rule is rigorously applicable only when the matrix is truly irreducible; i.e., there exists no relationship between the elements of the matrix other than those which are a consequence of the Hermitian character. This immediately excludes the application of the noncrossing rule to systems which contain hidden symmetries and accidental degeneracies.

In practice hidden symmetries are difficult to discover without first solving the system. In the two quantum systems H and H_2^+ where exact solutions are available for the electronic states, accidental degeneracies are found in both cases. Consequently the noncrossing rule is not applicable. In Fig. 2, it is seen that for the H_2^+ system, the adiabatic H_2^+ electronic states of the same symmetry (e.g., $2s\sigma_g$-$3d\sigma_g$, $3p\sigma_u$-$4f\sigma_u$) cross freely. For a general diatomic system where the questions of hidden symmetry and accidental degeneracy is not clear, the use of the noncrossing rule is uncertain.

In analyzing diatomic collisions, one observes that the details of the collision processes sometimes depend critically on the dynamic correlations between the asymptotic atomic states and the states of the united atoms. These dynamic correlations can be examined in the adiabatic representation. In this representation, the correlations between the separated- and united-atom states are given by the adiabatic electronic states. The noncrossing rule, however, sometimes clouds the correlation picture. To overcome this difficulty, a diabatic representation in which states of the same symmetry are allowed to cross is proposed by Lichten.[13]

Since the introduction of the diabatic states, there has been a great deal of discussion as to which basis — adiabatic or diabatic — should be used in calculations and in conceptual models. Rigorous calculations involving diabatic states require a quantitative definition of the states. Many different definitions may be made.[14] Since the exact H_2^+ electronic states of the same symmetry cross freely, the adiabatic-diabatic question does not exist in (p^+, H) collisions. For other collision systems, one expects that the details of the molecular states for $0 < R < \infty$ are less critical than the correct correlation of the separated and united atomic states in the $R = 0$ and $R = \infty$ limits.

Consider a diatomic system with separated-atom states f (here f denotes the product of atomic states of the separated atoms) and united-atom states $\mathcal{U}$. We may suppose that a set of molecular states φ can be generated from these atomic states by a unitary operator $\Omega(R_0, R_0')$,[15]

$$\varphi_\alpha(R_0) = \Omega(R_0, \infty) f_\alpha\,, \tag{5.1a}$$

$$\varphi_\alpha(R_0) = \Omega(R_0, 0)\mathcal{U}_\alpha\,, \tag{5.1b}$$

where the dependence on $\hat{R}_0$ and electronic coordinates are not explicitly shown. From the relation $\Omega(0,\infty) = \Omega(0,R)\Omega(R,\infty)$, we have

$$\mathcal{U}_\alpha = \Omega(0,\infty) f_\alpha\,. \tag{5.1c}$$

Thus the dynamical correlations between the separated and united atomic states may be represented by Ω. By the use of the relation

$$\sum_\alpha \varphi_\alpha\rangle\langle f_\alpha = \Omega(R_0,\infty) \sum_\alpha f_\alpha\rangle\langle f_\alpha = \Omega(R_0,\infty) \tag{5.2}$$

and the functional form of $\mathcal{V}_{\alpha\beta}$ given by Eqs. (2.17), the interactions $\mathcal{V}_{\alpha\beta}$ take the general form

$$\mathcal{V}_{\alpha\beta} = \langle f_\alpha | \tau^\dagger \Omega^\dagger V \Omega \tau - \tau^\dagger V' \tau | f_\beta\rangle\,, \tag{5.3}$$

where $\tau^\dagger$ and τ are the translational factors, and V and V' are the interaction operators, which are, for example, the operators in the matrix elements of $\mathcal{J}_{\alpha\beta}$ of (2.18). This suggests that the dynamical correlations between the separated and united atomic states can be introduced in the interaction $\mathcal{V}_{\alpha\beta}$ *without the explicit use of molecular states.*

B. Qualitative features of the nonadiabatic interactions

The current model for electronic transitions in atom-atom collisions is based heavily on the "coupling hypothesis" which states that the nonadiabatic transitions are directly correlated to the distance of the closest approach of the electron state energies. This hypothesis is the basic ingredient in the Landau-Zener model[16] for electronic transitions in slow collisions. The "coupling hypothesis" is supported by stationary phase arguments for cases where the phase of the nuclear wave function (coming from the diagonal interactions) oscillates everywhere much more rapidly than the nonadiabatic interaction except at the distance of closest approach of the energies. For cases where the nonadiabatic interactions are large at the distance of closest approach of the electronic states, the "coupling hypothesis" is automatically satisfied. Thus the study of the general behavior of the nonadiabatic interaction can provide valuable information on the region of validity of the "coupling hypothesis."

The radial couplings of the nonadiabatic interaction couple states of the same symmetry. The striking feature of the radial coupling is that their matrix elements are smaller between states that cross than between states that do not. A plot of these radial couplings (multiplied by a factor of R_0/z) is given in Fig. 12 together with the difference in electronic total energy (denoted by $\mathcal{E}$) and in kinetic energy (denoted by $\mathcal{K}$) between the corresponding states. It is seen that the maximum of the matrix elements between states that cross does not occur at the crossings. Between states that do not cross, the radial couplings are not largest at distance of closest approach. The radial coupling matrix elements, however, tend to be largest where the difference in the electronic kinetic energies is minimum. By the use of the virial theorem, the electronic kinetic energy $\mathcal{K}_\alpha$ may be expressed in terms of the electronic energy $\mathcal{E}_\alpha$ ($\mathcal{E}_\alpha = w_\alpha - W_\alpha$),

$$\mathcal{K}_\alpha = -\mathcal{E}_\alpha - R_0 \frac{\partial \mathcal{E}_\alpha}{\partial R_0}\,, \tag{5.4}$$

where the term $R_0 \partial \mathcal{E}_\alpha / \partial R_0$ is zero at $R_0 = 0$, $R_0 = \infty$,

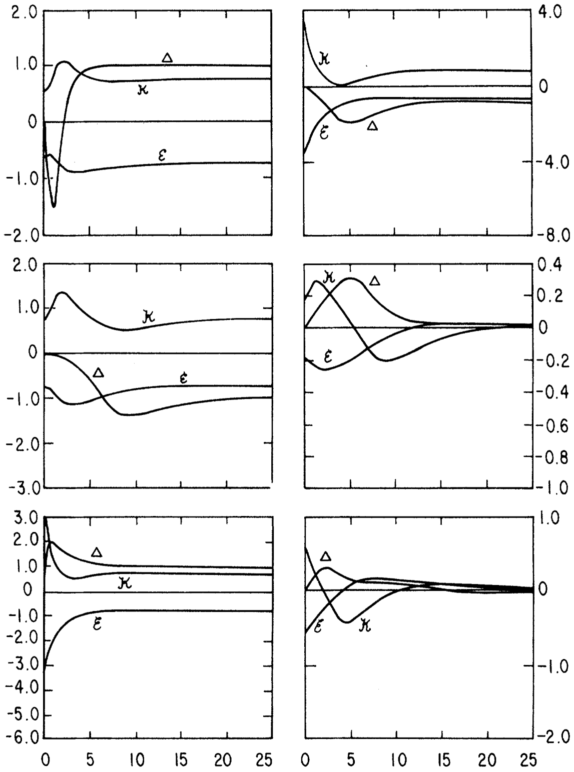

FIG. 12. Nonadiabatic radial matrix elements $\hat{z}\cdot(\varphi_\alpha, \vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0} \times 10 \times R_0/z$, the difference in total energy, and the difference in kinetic energy — Δ, $\mathcal{E}$, and $\mathcal{K}$, respectively — as a function of internuclear separation (in a_0) between the states (top to bottom, left to right) $2p\sigma_u$-$3p\sigma_u$, $2p\sigma_u$-$4f\sigma_u$, $1s\sigma_g$-$2s\sigma_g$, $1s\sigma_g$-$3d\sigma_g$, $3p\sigma_u$-$4f\sigma_u$, and $2s\sigma_g$-$3d\sigma_g$.

and $R_0 = R_e^{(\alpha)}$, the equilibrium distance of state α. Thus the closest approach of the total electronic energies is not in general at the same internuclear separation as the closest approach of the kinetic energies. These features of the radial coupling are not in favor with the "coupling hypothesis" except at low energies where the phases control the transition.

The rotational couplings which arise from the rotation of the quantization axis allow the coupling between states which differ by one unit in m. The rotational couplings, unlike the radial couplings, are dominated by their united-atom and separated-atom limits when the states are degenerate there. In Fig. 13, the rotational matrix elements (multiplied by a factor of R_0^2/B) are plotted together with the difference in electronic total energy (denoted by $\mathcal{E}$) and in kinetic energy (denoted by $\mathcal{K}$) between the corresponding states. It is seen that the $3d\sigma_g$-$3d\pi_g$ and $2p\sigma_u$-$2p\pi_u$ rotational matrix elements are largest in the united-atom limit where the states are degenerate. For the $2s\sigma_g$-$3d\pi_g$, $3p\sigma_u$-$2p\pi_u$, and $4f\sigma_u$-$2p\pi_u$ matrix elements between states that are degenerate in the separated-atom limit, the interactions are largest asymptotically. This is more apparent in Fig. 7 where the spurious long-range interactions are taken out so that the maximum is transmitted to the small R_0 region. Thus, the rotational couplings which couple only states of *different symmetry* are more compatible with the "coupling hypothesis."

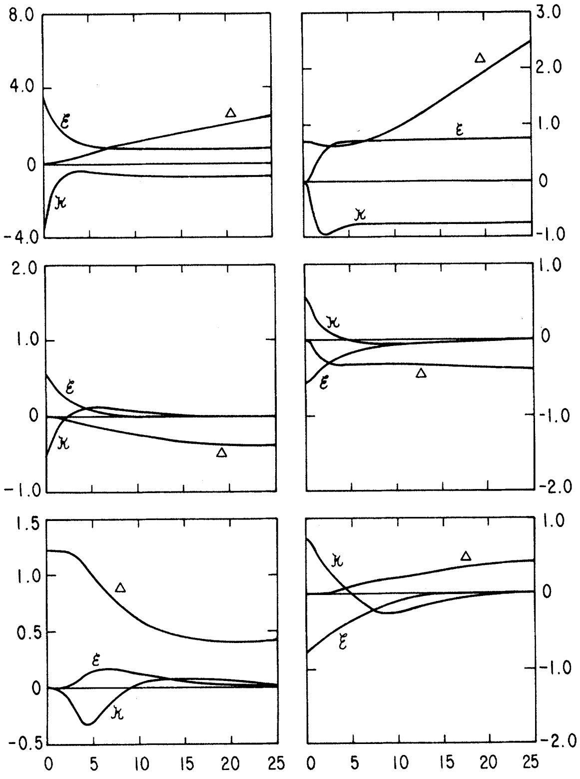

FIG. 13. Nonadiabatic rotational matrix element $\hat{z}\cdot(\varphi_\alpha, \vec{\nabla}_{\vec{R}_0}\varphi_\beta)_{\vec{R}_0} \times R_0^2/B$, the difference in total energy, and the difference in kinetic energy — Δ, $\mathcal{E}$, and $\mathcal{K}$, respectively —as a function of internuclear separation (in a_0) between the states (top to bottom, left to right) $1s\sigma_g$-$3d\pi_g$, $2s\sigma_g$-$3d\pi_g$, $3d\sigma_g$-$3d\pi_g$, $2p\sigma_u$-$2p\pi_u$, $3p\sigma_u$-$2p\pi_u$, and $4f\sigma_u$-$2p\pi_u$.

C. Phase-interference model

In general the rotational couplings are of shorter range than the radial couplings. From Figs. 6 and 7, it is seen that matrix elements vary significantly over a distance of ~$2a_0$ for the rotational couplings (including the B/R_0^2 factor) and a distance of ~$10a_0$ for the radial couplings. This difference in oscillation range can be significant in considering the interference with the phase of the nuclear motion. At low energies, this interference gives rise to the stationary-phase arguments. At higher energies, this interference continues to be important.

The interference can be examined from Eq. (1.2). After removing the asymptotic phases which do not depend on z, the function $\Lambda_{\alpha\beta}$ can be written as

$$\Lambda_{\alpha\beta} = i\upsilon_{\alpha\beta}[\cos\Phi_{\beta\alpha}(z,B) - i(z/|z|)\sin\Phi_{\beta\alpha}(z,B)], \tag{5.5}$$

with

$$\Phi_{\beta\alpha}(z,B) \cong \frac{1}{\upsilon}\int_0^{|z|}(\upsilon_\beta - \upsilon_\alpha)\,dz\,. \tag{5.6}$$

In the absence of the translational factors, $i\upsilon_{\alpha\beta}$ are essentially real. By iterating Q_α in Eq. (1.1), it can be shown that for interactions which are even functions of z, such as rotational couplings, the dominant contribution to Q_α comes from the $\cos\Phi_{\beta\alpha}(z,B)$ term. For radial couplings which are odd functions of z the $\sin\Phi_{\beta\alpha}(z,B)$ term gives the dominant contribution. With the inclusion of the translational factors and for $i\upsilon_{\alpha\beta}$ becoming complex, the picture is slightly modified but the qualitative feature remains much the same.

This suggests a simple qualitative model in which the radial couplings are weighted by the sine function of the nuclear phase $\Phi_{\beta\alpha}$ and the rotational couplings are weighted by the cosine function of the nuclear phase. The wavelength of the nuclear phase is proportional to the relative nuclear velocity [see Eq. (5.6)]. As the wavelength changes with velocity, the nuclear phase may interfere constructively or destructively with the phase of the coupling interaction which is essentially energy independent. By knowing the wavelength of the phase of the coupling interaction, the interference pattern can be investigated as a function of collision velocity.

A rough estimate of the wavelength of the phase of $iv_{\alpha\beta}$ may be obtained from plots where the interactions are plotted as functions of z and B for a given incident laboratory energy. The oscillations along z are confined within small B values. The shortest wavelength of the radial coupling corresponds to the wavelength of the nuclear phase for an incident energy of ~10 keV. Interactions which are even in z and singular at the origin will interfere constructively at all nonzero energies. Their strength and range will increase moderately as the wavelength of the nuclear phase increases. Interactions which are strongest away from the origin will have a much greater energy dependence. This is one of the fundamental differences between the rotational and radial coupling interactions.

In Fig. 14, the z dependence of the $2p\sigma_u$-$2p\pi_u$ rotational coupling and the cosine of the corresponding phase are shown for $B = 0.4a_0$ at laboratory energies of 0.5 and 10 keV. It is seen that in the range of the interaction the interference pattern does not change appreciably with energy. The z dependence of the $2p\sigma_u$-$3p\sigma_u$ radial coupling and the sine of the corresponding phase are shown in Fig. 15 for $B = 0.4a_0$ at laboratory energies of 0.5 and 10 keV. In this case it is seen that the strength of the radial coupling is greatly enhanced by the increase of the energy (laboratory) from 0.5 to 10 keV.

The $n = 2$ excitation in (p^+, H) collisions at low energies (< 1 keV) is due primarily to the $2p\sigma_u$-$2p\pi_u$ rotational coupling which gives rise to the $2p_{\cos\phi}$ excitation. The excitation of the $2p_0$ and $2s$ states is due to subsequent radial and rotational couplings. From the phase interference argument, we expect that the $2p_0$ and $2s$ production becomes significant at collision energies >10 keV.

APPENDIX: TRANSFORMATION FROM THE SPACE-FIXED TO THE ROTATING ATOMIC BASIS

If the asymptotic states are expressed in a fixed-space coordinate system, then no long-range interactions are present. If, however, the asymptotic states are expressed — as in the usual practice — in a coordinate system which rotates with the internuclear axis, then a certain type of long-range

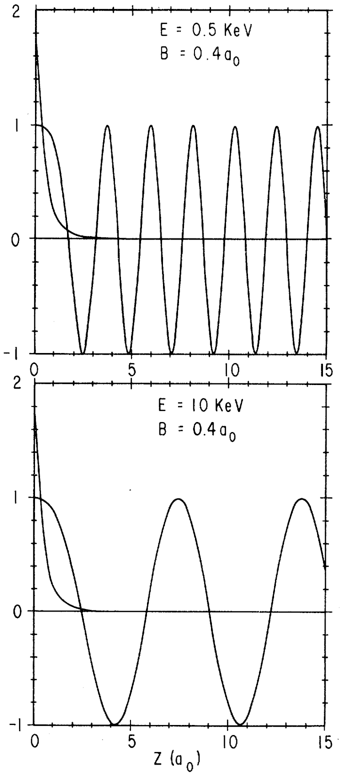

FIG. 14. z dependence of the rotational matrix element and cosine of the nuclear phase at $B = 0.4a_0$ for laboratory energies of 0.5 and 10 keV between the states $2p\sigma_u$-$2p\pi_u$.

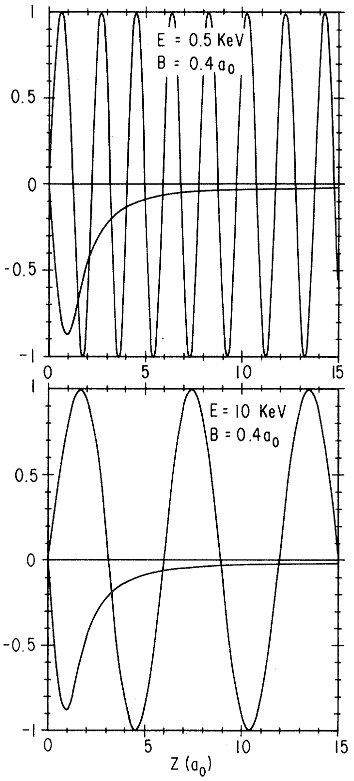

FIG. 15. z dependence of the radial matrix element and sine of the nuclear phase at $B = 0.4a_0$ for laboratory energies of 0.5 and 10 keV between the states $2p\sigma_u$-$3p\sigma_u$.

interaction will be present (see Sec. III D for detailed discussion). These long-range interactions appear explicitly in the transformation of the coupled equations for the nuclear wave function from a space-fixed to a rotating atomic basis.

With the use of eikonal approximation for the nuclear wave functions, the coupled equations given in Eqs. (2.16) take the form

$$iv\frac{d}{dz}\Psi_\alpha = \sum_\beta \mathcal{V}_{\alpha\beta}\Psi_\beta \,. \tag{A1}$$

Multiplying (A1) by g_α, summing over α, and noting that g_α are not a function of z gives

$$iv\frac{d}{dz}\sum_\alpha g_\alpha\Psi_\alpha = \sum_{\alpha\beta} g_\alpha \mathcal{V}_{\alpha\beta}\Psi_\beta \,. \tag{A2}$$

From the expressions of $\mathcal{V}_{\alpha\beta}$ given by Eqs. (2.23) and the equalities

$$\sum_\alpha |g_\alpha\rangle\langle g_\alpha| = \sum_\alpha |g'_\alpha\rangle\langle g'_\alpha| \,,$$

$$\sum_\alpha |f_\alpha\rangle\langle f_\alpha| = \sum_\alpha |f'_\alpha\rangle\langle f'_\alpha| \,, \tag{A3}$$

we have

$$\begin{aligned}\sum_{\alpha\beta} g_\alpha \mathcal{V}_{\alpha\beta}\Psi_\beta = {} & \sum_\alpha \sum_{s,t} g'_\alpha\rangle\langle g'_\alpha e^{i\mu\vec{\kappa}_s\cdot\vec{r}_1} g'_\alpha\rangle_{\vec{R}_1}\mathcal{J}_{st}\langle g'_t|e^{-i\mu\vec{\kappa}_t\cdot\vec{r}_2}\sum_\gamma g_\gamma\rangle_{\vec{R}_0}\Psi_\gamma \\ & + \sum_\alpha \sum_{st'} g'_\alpha\rangle\langle g'_\alpha e^{i\mu\vec{\kappa}_s\cdot\vec{r}_1} g'_s\rangle_{\vec{R}_1}\mathcal{J}_{st}\langle f'_{t'}|e^{i\mu\vec{\kappa}_t\cdot\vec{r}_2}\sum_{\gamma'} f_{\gamma'}\rangle_{\vec{R}_0}\Psi_{\gamma'} \,.\end{aligned} \tag{A4}$$

With the help of Eq. (A4) and the transformation given by (2.15), Eqs. (A2) take the form

$$iv\frac{d}{dz}\sum_\alpha g'_\alpha\Upsilon_\alpha = \sum_{\alpha\beta} g'_\alpha \mathcal{V}'_{\alpha\beta}\Upsilon_\beta \,, \tag{A5}$$

where $\mathcal{V}'_{\alpha\beta}$ are now expressed entirely in terms of the rotating atomic basis states. The coupled equations for the nuclear wave functions Υ_α are obtained by multiplying by g'_α and integrating over the electronic coordinates. We have

$$iv\frac{d}{dz}\Upsilon_\alpha = \sum_\beta \mathcal{V}'_{\alpha\beta}\Upsilon_\beta - iv\sum_\gamma \left\langle g'_\alpha \frac{d}{dz} g'_\gamma\right\rangle_{\vec{R}_0}\Upsilon_\gamma \,. \tag{A6}$$

Equation (A6) differs from (A2) by the presence of the $\langle g'_\alpha (d/dz) g'_\gamma\rangle$ term, in addition to that $\mathcal{V}'_{\alpha\beta}$ are expressed entirely in rotating atomic states.

If α is an s state, then the additional term will vanish for all γ. If α is a $2p_0$ or a $2p_{\cos\phi}$ state, then the matrix elements will not vanish. In particular, we have

$$\left(g'_{2p_0}(\vec{r}'_1)\frac{d}{dz}g'_{2p_{\cos\phi}}(\vec{r}'_1)\right) = +\frac{B}{R_0^2} \,, \tag{A7}$$

so that

$$iv\frac{d}{dz}\Upsilon_{2p_0}(R_1) = \sum_\beta \mathcal{V}'_{2p_0\beta}\Upsilon_\beta(R_1) + iv\frac{B}{R_0^2}\Upsilon_{2p_{\cos\phi}}(R_1) \,. \tag{A8}$$

The long-range interaction B/R_0^2 which is also present in the $\Upsilon_{2p_0}(R_2)$, $\Upsilon_{2p_{\cos\phi}}(R_1)$ and $\Upsilon_{2p_{\cos\phi}}(R_2)$ channel equations is due entirely to the transformation from the space-fixed to the rotating atomic basis.

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[10] See National Auxiliary Publications (NAPS) document No. 02581 for pages consisting of (i) the parameters p, A', and $\sigma=(R_0/p)-m-1$ for the lowest eight $H_2{}^+$ wave functions ($1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $2s\sigma_g$, $3p\sigma_u$, $3d\sigma_g$, $3d\pi_g$, $4f\sigma_u$) for $R_0=9.5$ to 150 a.u.; and (ii) the nonadiabatic electronic matrix elements between the adiabatic $H_2{}^+$ electronic state [Eqs. (3.8) and (3.9) which asymptotically tend to the $n=1$ or 2 atomic states], for $R_0=0$ to 150 a.u. These may be obtained from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, N.Y., N.Y. 10016. Remit with order for each NAPS document number $1.50 for microfiche or $5.00 for photocopies (for up to 30 pages). Make checks payable to Microfiche Publications.

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